Influence of ships emissions in the ultrafine particles pollution in an urban coastal air

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Resumen — **Experimental data (2008-2009) of particle number (N≥2.5 nm diameter) and black carbon (BC) concentrations and of gaseous pollutants recorded in the city of Santa Cruz de Tenerife was analyzed in order to asses the impact of ship emissions on the ultrafine particle (UFP) concentrations in coastal urban areas. The observed relationship between N and the other air pollutants, allowed segregating the contribution of vehicle exhaust and of ship emissions to the UFP concentrations in the urban ambient air.**

The influence of fresh vehicle exhaust emissions was mainly observed during the morning rush hours, resulting in high concentrations of BC, nitrogen oxides (NO_X) and UFP concentrations within the range 15 – 30 x10^3 cm^{-3}. A sharp decrease in BC and NO_X after the morning rush hours (not observed in the road traffic intensity) was associated with the entry of easterly marine air in the city. High concentrations of SO_2 and UFP were observed with the entry of this fresh marine air because of the inland transport of ship's plumes. During this period, the N/BC ratio exhibited an increase correlated with SO_2, wind speed, solar radiation and ozone concentrations. This suggests that a mechanism linked with the entry of marine air enriched in SO_2, probably also involving photochemical processes, is contributing to UFP concentrations within the range 35 – 50 x10^3 cm^{-3}.

Because of the daily inland transport of ship's plumes prompted by coastal breezes and because the high content of sulphur in these plumes, ships emissions emerge as a major source of UFP in coastal cities, frequently exceeding the contribution of the vehicle exhaust emissions.

Palabras claves— **Ultrafine particles, ship emissions, vehicle exhaust.**

I. Introduction

Air quality impairment due to ultrafine particles (<100 nm diameter) pollution has become in a topic of great interest within the context of environmental sciences and public health protection [Oberdörster *et al.*, 2004; Araujo *et al.*, 2009] with large uncertainties in both areas.

UFP typically account for 80–90% of the total particle number concentration in urban air [Wehner *et al.*, 2002, Rodríguez *et al.*, 2007, Mejía *et al.*, 2008]. Most of studies attribute the main origin of UFP in urban ambient air to: a) Vehicle exhaust emissions. Fresh particles emitted by vehicle exhausts tend to be bimodal, exhibiting a nucleation (<20 nm; mostly constituted by sulphuric acid droplets, formed during the dilution and cooling of the exhaust and coated by condensed sulphate and/or hydrocarbons) and a carbonaceous (50–200 nm; predominantly made up of soot, absorbed organic material and other trace elements formed in the engine and directly emitted in the solid phase) mode. It is considered that sulphuric acid gas molecules play a key role as initial cluster, whereas vapors involved in the growth processes are linked to photo-oxidation of SO_2 and/or organic vapors.

Most of studies on urban air quality and UFP have focused on vehicle exhaust emissions even if it is well known that other sources may also contribute. We have focused on the UFP pollution due to ship emissions. These emissions impact on human health [Corbett *et al.*, 2007a] and contribute to damage the environment [Derwent *et al.*, 2005] and climate [Lauer *et al.*, 2007; Stern *et al.*, 2007; Lack *et al.*, 2009]. Ship emissions are known as one of the least regulated source of pollutants [Eyring *et al.*, 2005]. Primary particles emitted by ships are constituted by a complex mixture of elemental and organic carbon, sulphate condensed onto ashes [Petzold *et al.*, 2004; Kasper *et al.*, 2007] and trace metals [e.g. V and Ni; Viana *et al.*, 2009]. Moreover, emissions of volatile organic compounds and sulfur dioxide result in the formation of secondary particles by nucleation and condensation processes [Petzold and Schönlinner, 2004]. Because of these features, the size distribution of particles within ship's plumes may covers from the nucleation to the coarse mode (e.g. 0.005 to >3 μm; [Petzold *et al.*, 2004; Kasper *et al.*, 2007]).

Air quality impairment due to PM_{10} and $PM_{2.5}$ pollution by ships is already well characterized [Agrawal *et al.*, 2008; Moldanová *et al.*, 2009]. In this study we have focused on quantifying the contribution of ship emissions to the UFP concentrations in the urban ambient air in coastal cities.

Results show that, because of the daily inland transport of ship's plumes prompted by coastal breezes and because the high content of sulfur in these plumes, ships emissions emerge as a major source of UFP in coastal cities, frequently exceeding the contribution of the vehicle exhaust emissions.

II. Methodology

A. Study area

The study was performed in Santa Cruz de Tenerife (28º28'22" N 16º14'19" W; Canary Islands, Spain). The main sources of pollutants in the city are: a) vehicle exhaust emissions; b) emissions of ships at the East of the city; and c) a crude oil refinery located at the SW of the city, at about 3 km far from the measurement site. These emissions only reached the station under synoptically driven Southern winds, which occurs less than 10% of the days per year. Data collected during fumigations of the plumes of the refinery were identified and not included in the analysis performed in this study.

Pollutant transport in this urban area is highly influenced by the development of coastal breezes (Figure 1B, discussed below). From 10 to 17 GMT, the landward breeze circulation favors the inland transport of the pollutants emitted in and near the shore. At night, a slight seaward airflow occurs.

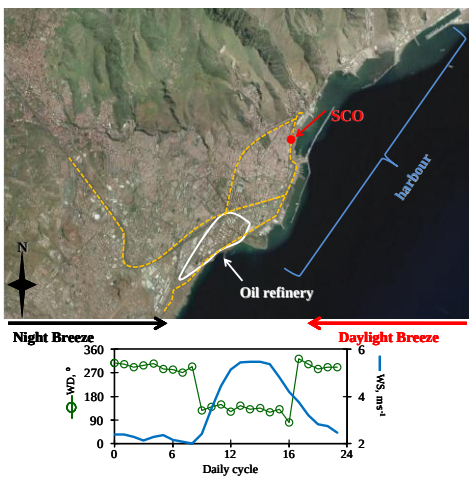

Fig. 1. A) Map of the city of Santa Cruz de Tenerife highlighting the location of the SCO station (red dot), main in and out roads (yellow dashed lines), the oil refinery (white line) and the harbor (blue line). B) Daily sea-land breeze cycle.

B. Measurements

Measurements were performed at the so-called "Santa Cruz Atmospheric Observatory" (SCO; www.izana.org). Data of trace gases concentrations (reference European methods for NO_X, SO_2, O_3 and CO), of N and BC concentrations and of meteorological parameters (radiation, wind speed and direction) collected from April 2008 to December 2009 were used. A mass absorption efficiency σ = 9.79 (± 0.45, r^2=0.89) $m^2 \cdot g^{-1}$ was used based on previous studies of our group [Fernández-Camacho *et al.*, 2010; Reche et al., 2011].

Data availability for the period 2008 - 2009 was 67% for NO_X, 98% for SO_2, 98% for O_3, 70% for N and 83% for BC. Additionally, road traffic intensity (number of vehicles/hour) was monitored by the city council staff at the Anaga Avenue.

C. Segregation of particle number components

The contribution of the different sources and processes to the UFP concentrations in the urban ambient air, is quantify with the methodology developed by Rodríguez and Cuevas (2007). In this technique, the number concentration N is split in two components:

$$N1 = S1 \times BC \quad (1)$$

$$N2 = N - N1 \quad (2)$$

where the S1 value observed in the morning (7.9×10^6 particles / ngBC) was used. When road traffic is the predominant source of BC, represents the minimum primary emissions of the vehicle exhaust and accounts for the emissions of soot mode particles and those components that nucleate immediately after emission (those which are in the aerosol phase under typical ambient air conditions, Kittelson *et al.*, 1998; Burtscher, 2005; Arnold *et al.*, 2006; Rose *et al.*, 2006). Component N2 accounts for those processes resulting in N / BC ratios above S1 by enhancement in the new particle formation rates due to increased nucleation and / or growth rates to detectable sizes (≥2.5 nm in our case) in different contexts: during the dilution and cooling of the vehicle exhaust emissions [Casati *et al.*, 2007], in ambient air due to photochemistry [Woo *et al.*, 2001; Wehner *et al.*, 2002], and/or in aerosol precursor plumes [Fernández-Camacho *et al.*, 2010].

III. Results and Discussion

A. Sources of UFP

Figures 2A-2E shows hourly mean values of particles (N and BC) and gaseous (CO, SO_2 and NO_X) pollutants, road traffic intensity (number of vehicles / hour), road traffic intensity / wind speed ratio, N/BC ratio and solar radiation for working days (calculated for each month of the year). High BC, CO and NO_X concentrations were registered dur-

ing the morning rush hours due to vehicle exhaust emissions (07:00 – 09:00 GMT, Figs. 2A, 2B and 2D). The abrupt decrease in the concentrations of pollutants after 10:00 GMT is not observed in the road traffic intensity. This decrease is prompted by the air mass renewal due to the blowing of the coastal inland sea breeze since 10:00 GMT (Fig. 1B). The high correlation between BC, NO_X and CO with the road traffic intensity / wind speed ratio (Fig. 2B) indicates that these pollutants are predominantly influenced by fresh vehicle exhaust emissions and the air mass renewal prompted by the inland sea breeze blowing. This sea regime is characterized by inland (westward) sea breeze blowing (4 – 5 $m \cdot s^{-1}$) during daylight (10:00 - 17:00 GMT) and a slight seaward (eastward) airflow at night (~2 $m \cdot s^{-1}$, Fig. 1B).

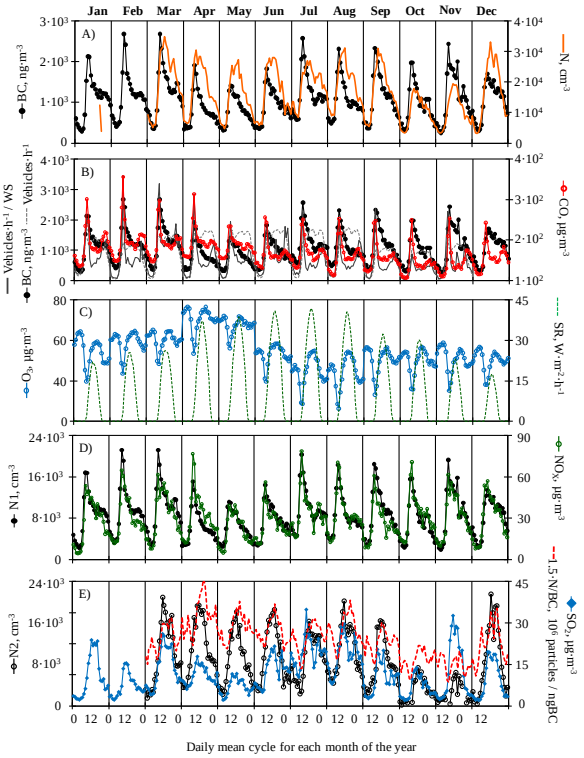

Fig. 2. Hourly mean values of particles (N and BC) and gaseous pollutants concentrations (NO_X, SO_2 and O_3), and of the road traffic intensity (number of vehicles/hour), wind speed, the road-traffic intensity/wind speed ratio, of the N/BC ratio, N1, N2 and solar radiation for working days for each month of the year.

High values of SO_2 are registered during the easterly inland sea breeze blowing period (10:00 – 17:00 GMT; Fig. 1E). SO_2 and O_3 increase simultaneously with solar radiation due to the entry of fresh marine air into the city prompted by solar heating (Figs. 2C and 2E). This is attributed to the inland transport of ship plumes from the harbor.

The abrupt increases in particle number concentrations (N) during the morning rush hours (correlated with NO_X, CO and BC) evidence a high influence of vehicle exhaust emissions in this period (Figs. 2A-2B). However, concentrations of N reach a maximum (Fig. 2A, 11:00 – 12:00 GTM) latter than BC concentrations (07:00 – 09:00 GMT). The simultaneous increases in SO_2, N / BC ratio, solar radiation and O_3 during the inland sea breeze blowing period suggests that photochemically induced UFP formation in ship plumes may be contributing to the N concentration in the urban ambient air (Figures 2C and 2E). This additional mechanism of UFP supply may accounts for the fact that the slope S1 is higher during the inland sea breeze period ($14.5 \cdot 10^6$ particles / ngBC, Fig. 2B) than during the morning rush hours ($7.9 \cdot 10^6$ particles / ngBC, Fig. 3). This relationship between N and BC is typically observed in urban ambient air (e.i. Huelva, Barcelona, Milan, Bern, Lugano and London; Rodríguez and Cuevas, 2007; Fernández-Camacho et al., 2010, Reche et al., 2011).

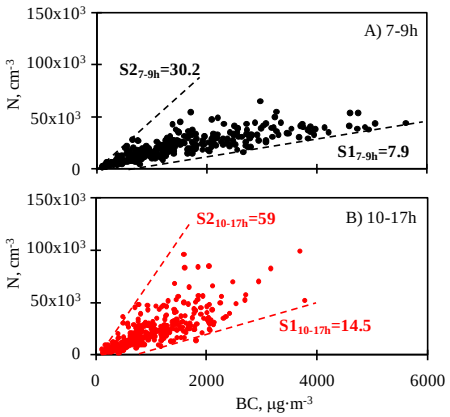

Fig. 3. Hourly mean values of N versus BC particle concentrations at different times of the day in Santa Cruz City. S1 (10^6 particles / ngBC): minimum N-vs.-BC slope.

The daily evolution of N1 was similar to that of NO_X, with a maximum value from 07-09 GMT on working days, whereas N2 was similar to that of SO_2, with high values during the inland sea breeze blowing (Figs. 2F-2G). These correlations are support by the results obtained in a Principal Component Analyses (PCA) followed by varimax rotations performed with 1-h average data, for two periods: 07-09 GMT and 10-17 GMT. Eigenvalues > 1 and a maximum number of principal components equal to 4 were set (Table 1).

Table 1. Factor loading of the Principal Components Analysis (followed by a varimax rotation) obtained with hourly data in the morning (07:00–09:00 GMT) and noon-afternoon (10:00–17:00 GMT). Factor loadings with absolute values ≥ 0.7 are in bold. RTI / WS: road traffic intensity / wind speed.

	07-09 GMT		10-17 GMT	
	PC 1	PC 2	PC 1	PC 2
	vehicles 1	vehicles 2	ships	vehicles
N1	**0.81**	0.44	**0.78**	0.35
N2	-0.05	**0.89**	**0.79**	-0.12
CO	**0.90**	0.04	0.00	**0.80**
SO_2	0.21	**0.86**	**0.90**	-0.08
NOx	**0.83**	0.46	**0.86**	0.24
RTI/WS	**0.82**	-0.18	0.09	**0.76**
Variance	48 %	33 %	46 %	24 %

B. Contribution of ship emissions to UFP concentrations in urban ambient air

The contribution of N1 and N2 to N showed significant variations in the vehicle exhaust and ship events. The higher N2 load in N during the 10:00 – 17:00 GMT period, is associated with an increase in SO_2 (3 and 58 μg·m^{-3}, Fig. 4) concentrations. The correlated evolution of N2 and SO_2 during ship events (Figures 3B2) evidences the role of ultrafine particle formation in the SO_2 plumes. High total number concentrations associated with burst of nucleation mode particles during fumigations of SO_2 plumes were observed by Stanier et al. (2004) and Cheung et al. (2011). The higher N1 load in N during the morning rush hours evidence a higher load of soot, whereas the higher N2 load during ship events are attributed to the presence of sulfate.

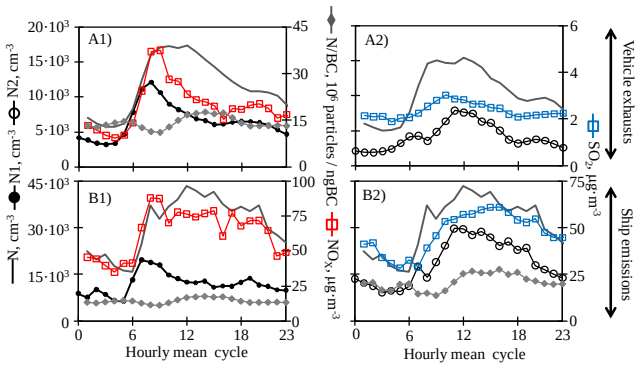

Fig. 4. Daily evolution of gaseous (SO_2 and NO_X) and particle (N, N/BC, N1 and N2) concentrations for typical events of vehicle exhaust and ships emissions.

In Figure 5 the hourly mean N data is classified from the highest to the lowest value, highlighting the contribution of N1 and N2 to N (Figs. 5A1-5B2). The associated SO_2 and NO_X concentrations (Figs. 5C1-5D2) recorded during the morning rush hours and during the inland sea breeze blowing period are also shown. Under the predominant influence of the vehicle exhaust emissions in the morning, N shows a monotonic increase with NO_X (Figs. 5A1 and 5C1). In this period, the contribution of N1 and N2 to N is very close, ranging between 40 - 60 % each for the whole percentile range (Fig. 5B1). Under the influence of ship emissions during the inland sea breeze blowing period, N shows a monotonic increase with SO_2 and NO_X (Figs. 5A2, 5C2 and 5D2), and it may reach much higher concentrations than in the morning (~twice; Fig. 5A2). The increase in N concentrations is prompted by an enhancement in N2, whose contribution accounts for 46 ± 16 %, 58 ± 14 % and 70 ± 14 % for the N percentiles ranges <20th, 20–80th and >80th (Figure 5B2). These much higher N2 concentrations are prompted by the much higher SO_2 concentrations under the influence of ship plumes than vehicle exhausts (up to 10 time higher; Figs. 5D1 and 5D2).

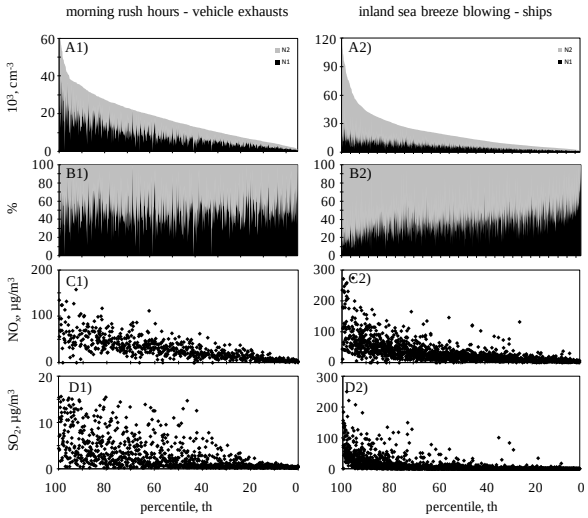

Fig. 5. Hourly mean values of total number concentration (N=N1+N2) classified from the highest (100th) to the lowest (0th) value. The contributions of N1 (black) and N2 (grey) to N, in absolute (cm^{-3}; A-E) and relative (%; B-F) concentrations are highlighted. NO_x (C-G) and SO_2 (D-H) concentrations associated with the decreasing N values (from 100th to 0th) are plotted.

IV. Conclusions

Air quality impairment due to UFP pollution has become in a matter of concern due to adverse effects of these particles on human health. Up to the date, most of studies on ultrafine particles in urban air have focused on vehicle exhaust emissions. It this study we have focused on the impact of ship emissions on the ultrafine particles concentrations in downwind urban areas.

A data set of number of particles coarser than 2.5 nm (N), particulate black carbon concentrations (BC), gaseous pollutants (SO_2, NO_X and O_3) and meteorological parameters recorded in a coastal city has been analyzed. Results shows that the impact of vehicle exhaust and ship emissions can be segregated. Particle number concentration (N) was split into two components: N = N1 + N2, where N1 is linked to vehicle exhaust emission of carbonaceous material (including light absorbing matter) and components nucleating immediately after the emission, whereas N2 is linked to new particle formation due to SO_2 emissions (from vehicle exhaust and ship).

During the morning rush hours of the working days, when ultrafine particles are linked to vehicle exhaust emissions, N showed concentrations within the range 15 – 30 $x10^3$ cm^{-3}. In this context, N2 accounted for 55.65% of N, being the reaming fraction linked to N1. The inland sea breeze blowing results in a drop of concentrations of the gaseous and particulate pollutants emitted by vehicle exhausts. However, this airflow results in the inland transport of the ship's plumes into the city. This results in an increase in the concentrations of ultrafine particles and SO_2 during the inland sea breeze blowing. In this period, N typically shows concentrations within the range 35 – 50 $x10^3$ cm^{-3}, when N2 accounts for 65 - 70 % of N. This N2 fraction clearly shows an increasing trend with SO_2 concentrations. The results of this study shows that ship emissions may results in much higher concentrations of ultrafine particles that vehicle exhaust emissions.

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